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Signature

TO ALL WHOM IT MAY CONCERN:

Be it known that we, **SATORU MATSUBAYASHI**, a citizen of Japan, whose post office address is 340-301, Koedo-cho, Utsunomiya-shi, Tochigi-ken, Japan; and **MASAHIRO FUKIMBARA**, a citizen of Japan, whose post office address is 44-1, Miyuki-cho, Utsunomiya-shi, Tochigi-ken, Japan, have invented an improvement in

**LINERLESS INK-JET RECORDING ADHESIVE LABEL**

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**CROSS REFERENCE TO RELATED APPLICATION(S)**

[0001] This application is a national stage application of PCT Application No. PCT/JP2004/016283 which was filed on October 27, 2004 and published on May 6, 2005 as International Publication No. WO 2005/040297 (the "International Application"), the entire disclosure of which is incorporated herein by reference. This application claims priority from the International Application pursuant to 35 U.S.C. § 365. The present application also claims priority under 35 U.S.C. § 119 from Japanese Patent Application No. 2003-369033, filed October 29, 2003, the entire disclosure of which is incorporated herein by reference.

10 **FIELD OF THE INVENTION**

[0002] The present invention relates to a linerless ink-jet recording adhesive label which does not require a release paper.

**BACKGROUND INFORMATION**

15 [0003] Recently, due to the use of personal computers and digital cameras has increased, an adhesive label using a recording sheet capable of full-color printing as the substrate thereof has become widely used.

[0004] In particular, a utilization of an ink-jet recording adhesive label using an ink-jet recording sheet has been increasing, because the label enables easy printing and has a good flexibility in small lot recording.

20 [0005] In this ink-jet recording scheme, due to a head nozzle of a printer and a recording surface not contacting one another, it may be advantageous that the recording can be performed on a label adhered to an adherend having a rough surface or a curved surface.

[0006] The ink-jet recording adhesive label can generally be composed of a substrate such as a high-quality paper or an ink-jet recording sheet having a support and an ink-jet recording layer formed on the support, and an adhesive layer and a release paper provided in this order on the rear surface of the substrate.

5 [0007] There is an environmental problem common to most if not all adhesive labels having a release paper (without being limited to the ink-jet recording adhesive labels) in which a significant amount of release papers are disposed of as refuse after adhering the labels to the adherends thereof.

[0008] Because numerous release papers cannot be repulped using conventional  
10 equipment for recycling used paper, they have been incinerated or dumped in a landfill. Moreover, because the paper thickness increases by corresponding amounts of the release paper used in the label, it may be problematic that the length of a rolled adhesive label which can be built in a label-printer may be limited, and so enlargement of the printer-size or frequent replacement of a roll of the adhesive label may be needed.

15 [0009] In order to solve the problem caused by the use of the release paper, a heat-sensitive recording adhesive label can be provided in which a release agent layer is facilitated on the surface of a heat-sensitive recording layer of a heat-sensitive recording sheet. In this manner, it is possible to eliminate the requirement of the release paper has been described in, for example, Japanese Patent Application, Second Publication No. Hei 4-15110.

20 [0010] In addition, a linerless ink-jet recording adhesive label can be provided in which the release paper is not required by using a particular release agent, and which has a suitability for ink-jet recording as described in, for example, Japanese Patent Application, First publication No. 2001-139900.

[0011] As provided in Japanese Patent Application, Second Publication No. Hei 4-15110, although the release agent layer is provided on the surface of the heat-sensitive recording layer, it may difficult to apply this layer to the ink-jet recording.

[0012] In general, a compound having a basic skeleton of polydimethylsiloxane containing many nonpolar methyl groups is used as a release agent so as to enable the adhesive layer to be easily exfoliated. Accordingly, when a release agent layer is conventionally formed on the surface of the ink-jet recording layer, ink droplets spluttered by an ink-jet printer are repelled, and thus the recording may not be performed.

[0013] When applying a small quantity of the release agent, the suitability for ink-jet recording can be maintained, but the peeling properties may significantly decrease.

[0014] Although the ink-jet recording label described in Japanese Patent Application, First Publication No. 2001-139900 has no explicit known problem when conventionally used, the force preferred for peeling likely slightly increases when a long time has passed after the end of the production. When the peeling force increases, defects in operating a printer-labeler or deterioration of the suitability for ink-jet recording may be sustained. Recently, the case in which the ink-jet recording label is used after being stored for a significant period of time has been increasing in accordance with the broader use thereof. Accordingly, a linerless ink-jet recording label having an enhanced performance free from the increased force required for peeling even over time may be preferred.

## **SUMMARY OF EXEMPLARY EMBODIMENTS OF THE INVENTION**

[0015] Based on the preferences to avoid or reduce the above-described deficiencies, exemplary embodiments of the present invention are provided. One of the objects of the present invention is to provide a linerless ink-jet recording adhesive label having a suitability for ink-jet

recording even though a release paper is not needed in consideration of the environment, while such label may have excellent adhesive and peeling properties that may be substantially or completely free from the increased force used for peeling over time.

[0016] In order to achieve the above-mentioned object and other objects in accordance with the exemplary embodiments of the present invention, a release agent can be used which contains as its main component, a polyvinyl alcohol containing a long-chain alkyl group, an amino-alkyd resin containing a long-chain alkyl group, and/or a polyethylenimine containing a long-chain alkyl group (instead of a silicone-based release agent conventionally and widely used as a release agent), or any combination thereof. For example, such release agent can be a material that does not deteriorate the suitability for ink-jet recording, but exhibits peeling properties free from the increase of the force required for peeling even over time.

[0017] According to one exemplary embodiment of the present invention, the above-described problems can be solved by using an adhesive containing fine spheres for an adhesive layer, and combining this adhesive with the release agent.

[0018] For example, the exemplary embodiments of the present invention provide a linerless ink-jet recording adhesive label which can include an ink-jet recording sheet as a substrate, a release agent layer provided on the front surface of the substrate, and an adhesive layer provided on the rear surface of the substrate. The release agent can include the release agent layer which can have at least one polymer of a polyvinyl alcohol containing a long-chain alkyl group, an amino-alkyd resin containing a long-chain alkyl group, and a polyethylenimine containing a long-chain alkyl group, and/or the adhesive layer is formed by an adhesive containing fine spheres. According to another exemplary embodiment of the present invention, a solid content of the fine spheres may be provided which is 20 to 80% by mass of the adhesive containing fine spheres.

[0019] In a further exemplary embodiment of the present invention, a sticking and printing method can be provided. For example, the linerless ink-jet recording adhesive label can be formed

into a wound body in a roll shape by adhering the adhesive layer to the release agent layer present at the rear of the adhesive layer. The wound body may be conveyed while being rewound by using a conveyer and is stuck on a material to be stuck, and printing is performed on the surface of the release agent layer using an ink-jet ink.

- 5    [0020]        These and other objects, features and advantages of the present invention will become apparent upon reading the following detailed description of the exemplary embodiments of the present invention, when taken in conjunction with the appended claims.

### **DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS OF INVENTION**

- 10    [0021]        According to exemplary embodiments of the present invention, an ink-jet recording sheet used as the substrate can include sheets conventionally used as ink-jet recording sheets regardless of the kinds of sheets and existence of an ink-jet recording layer.

- [0022]        For example, a high-quality paper (acid paper, neutralized paper), medium-quality paper, coated paper, resin-laminated paper, and the like can be used alone or in combination as the  
15    substrate. Also, the substrate may be formed by using one or more of these as a support, and providing an ink-jet recording layer that is mat, lustrous, extremely lustrous, or the like on one surface of the support.

- [0023]        In order to increase the strength of the surface of the substrate on which an adhesive is applied, to improve adhesion properties between the substrate and an adhesive layer, and/or to  
20    prevent the adhesive from infiltrating into the substrate and causing deterioration of adhesive function, a barrier layer may be provided. The barrier layer may be a layer in which a water-soluble polymer such as polyvinyl alcohol, starch, or the like, and/or a pigment are(is) mainly contained, or in which a resin mainly containing polyester, polyurethane, acryl polyol, polyethylenimine, polyacrylamine, polyacrylic acid ester, modified polyolefin, oxazoline,

ethylene-vinyl acetate copolymer, vinyl chloride-vinyl acetate copolymer, or the like is used alone or in combination therewith.

[0024] Also, a single layer or plural layers in which a reactive curing agent such as isocyanate compounds, epoxy compounds, or the like is added may be provided, as needed.

5 [0025] According to an exemplary embodiment of the present invention, a release agent can be provided which can include a release agent layer that may be provided on the front side of the substrate. For example, the release agent layer can include at least one polymer of a polyvinyl alcohol containing a long-chain alkyl group, an amino-alkyd resin containing a long-chain alkyl group, and/or a polyethylenimine containing a long-chain alkyl group. Among these polymers,  
10 one can mainly contain a polyvinyl alcohol that may preferably include a long-chain alkyl group. When the substrate has an ink-jet recording layer, the front side of the substrate can mean the ink-jet recording layer side. When the substrate does not have an ink-jet recording layer, the front side can mean the side on which the release agent layer is provided.

[0026] While a silicone-based release agent generally used exhibits high peeling  
15 properties, it can repel ink droplets because of its inherent water repellency, and thus would scarcely have the ink-absorbability and ink-fixable property. Accordingly, a non-silicone-based release agent which does not deteriorate suitability for ink-jet recording can be used according to an exemplary embodiment of the present invention.

[0027] Since the non-silicone-based release agent is generally poor in peeling properties, it  
20 is preferable that nonpolar groups are aligned on the surface of a coated layer formed by coating the non-silicone-based release agent so as to exhibit the peeling properties from the adhesive.

[0028] The polyvinyl alcohol containing a long-chain alkyl group has a polyvinyl alcohol which is rich in hydrophilic property as its main chain and a long-chain alkyl group which is rich in peeling property as its side chain. Accordingly, it is possible to demonstrate both the peeling

property and suitability for ink-jet recording by introducing a long-chain alkyl group as the side chain into a polyvinyl alcohol.

[0029] In order to exhibit desired characteristics, it may be preferable that the long-chain alkyl group of the polyvinyl alcohol containing the long-chain alkyl group has about 10 to 30 carbon atoms. When the number of the carbon atoms may be at least about 10, good peeling properties are demonstrated, while when the number is at most about 30, the suitability for ink-jet recording would likely not be deteriorated.

[0030] The amount of the release agent in the release agent layer may preferably be within a range from about 0.1 to 5.0 g/m<sup>2</sup>, more preferably within a range from about 0.5 g/m<sup>2</sup> to 3.0 g/m<sup>2</sup>, and even more preferably within a range from about 0.7 to 1.5 g/m<sup>2</sup>. When the amount of the release agent is at least 0.1 g/m<sup>2</sup>, good peeling properties can be exhibited, while when the amount is at most about 5.0 g/m<sup>2</sup>, good suitability for ink-jet recording can be maintained. Thus, the problems such as ink-repelling, rubbing, and the like would likely not be caused.

[0031] For example, when the amount of the coated release agent is controlled within a range from about 0.7 to 1.5 g/m<sup>2</sup>, an appropriate pinhole is formed on the surface on which the release agent is coated. Thus, a label having the most favorable balance between the peeling properties and the ink-absorbability can be obtained. Moreover, in the method in which printing is performed after a label is stuck on a material to be stuck, labels which scarcely cause ink-repellency, blurring, and the like can be obtained, even when printing is performed using a particular printer in which a head nozzle thereof is separated from the printing surface by a few centimeters so as to perform printing on various materials to be stuck having various size and thickness.

[0032] In order to form the release agent layer on the surface of the substrate, a method in which a coating solution of the release agent is applied on the surface of the substrate can be used.



[0033] The coating solution of the release agent may be a solvent-based solution, emulsion-based solution, or solventless solution and is not particularly limited, and the emulsion-based solution may be preferably used. Since the solvent-based release agent exhibits an extremely rapid infiltration rate, when the agent is applied on a high-quality paper, for example, the agent infiltrates into the opposing surface of the paper, as a result of which both surfaces of the paper exhibit peeling properties and may not exhibit sufficient adhesion properties between the adhesive and the substrate. When the emulsion-based release agent coating solution is used, it is preferable that the concentration of the release agent coating solution be within a range from about 1 to 40%, and the viscosity thereof at about 25°C be approximately within a range from about 5 to 500 mPas in consideration of the infiltration of the release agent into the ink-jet recording sheet, uniformity of the coated surface, and ease of control of the amount of coating.

[0034] To the coating solution of the release agent, various auxiliary agents such as dyes, pigments, moistening agents, antifoaming agents, foam inhibitors, dispersants, antistatic agents, leveling agents, lubricants, thickeners, antioxidants, ultraviolet absorbers, or the like, may be arbitrarily added as needed, unless desired effects are deteriorated.

[0035] The exemplary method for applying the coating solution of the release agent is not limited, and conventional applicators such as a spray, Mayer bar coater, kiss roll coater, lip coater, direct roll coater, offset roll coater, gravure roll coater, reverse roll coater, air knife coater, and the like may be arbitrarily used, for example. The amount of coating may be controlled so that the dry mass may be within a range described above.

[0036] Further, the adhesive layer provided on the rear surface (the surface opposite to the release agent layer) of the ink-jet recording sheet can be described. According to an exemplary embodiment of the present invention, the adhesive layer may be formed by an adhesive containing fine spheres.

[0037] An adhesive which is a base is not particularly limited, and any adhesives conventionally used for adhesive labels can be used. Among these adhesives, an acrylic acid ester-based adhesive containing polyacrylic acid as the main component thereof is preferably used, because the adhesive has various types of performance which are available as needed and exhibits  
5 a good compatibility with fine spheres composed of an elastomer copolymer mainly containing an acrylic acid ester described below. The type of the acrylic acid ester-based adhesive may be a strongly caking type, a commodity type, a repeelable type, or the like, and is not particularly limited.

[0038] Although the adhesive may be a single-component type or a curing type of two or  
10 more-components, the one-component type may be preferable. This is because the curing type of two or more-components is very soft and rich in flowability until the adhesive is cured after coating, and so the adhesive is infiltrated into the surface of the ink-jet recording sheet, as a result of which multidelamination or deterioration of the suitability for ink-jet recording may be easily caused, even if the release agent layer is formed.

15 [0039] The fine spheres are preferably elastic fine spheres composed of elastic bodies.

[0040] As such elastic fine spheres, other materials may be used provided that such materials are composed of an elastomer, and polybutadiene-based, styrene-butadiene-based, polyisoprene-based elastomers, elastomer copolymers mainly containing acrylic acid ester and/or the like can be used, and cross-linked materials may also be used as needed. Among these  
20 compounds, the fine spheres composed of the elastomer copolymer mainly containing acrylic acid ester are preferably used.

[0041] The elastomer copolymer mainly containing acrylic acid ester may be a copolymer of at least one acrylic acid ester and a monomer having a carboxyl group or an ionic monomer, and may further contain a component originated from a monomer that is copolymerizable therewith.

[0042] As the fine spheres, any type such as one having or not having adhesion properties in itself, one containing or not containing a binder component, or the like may be used.

[0043] When the content of the component originated from the monomer having a carboxyl group or the ionic monomer is no less than the determined content, the fine spheres can become adhesive, while when the content is less than the determined content, the fine spheres may become non-adhesive.

[0044] Examples of acrylic acid ester include n-butyl acrylate, i-butyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, i-octyl acrylate, n-nonyl acrylate, i-nonyl acrylate, n-decyl acrylate, and the like. Examples of the monomer having a carboxyl group include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid, citraconic acid, and the like.

[0045] Examples of the monomer copolymerizable with these include alkyl acrylates having a C1 to C3 alkyl group, alkyl methacrylates such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, and the like, maleates such as dimethyl maleate, di n-butyl maleate, and the like, fumarates such as dimethyl fumarate, di n-butyl fumarate, and the like, amides containing an unsaturated group such as acrylamide, methacrylamide, and the like, monomers having an amino group, a hydroxyl group, an epoxy group, a mercapto group, and/or a radical-polymerizable unsaturated bond, and the like.

[0046] It may be preferable that the glass transition temperature of the elastomer copolymer mainly containing acrylic acid ester be at most about -10°C.

[0047] It may be preferable that the number-average particle diameter of the fine spheres be controlled within a range from about 20 to 50  $\mu\text{m}$ . When the average particle diameter is less than about 20  $\mu\text{m}$ , only a few of the fine spheres generally protrude out of the surface of the adhesive, and fine spheres are likely flattened when a tape-like ink-jet recording adhesive label is

stored for a long time, as a result of which multidelamination, defect in operating a printer, and deterioration of the suitability for ink-jet recording may occur.

[0048] Although as a countermeasure against these issues, it is possible to softly roll the tape-like label, this causes a defective appearance of the rolled tape, such as gapping, deformation, or the like, but may not be preferable. In addition, although it is possible to decrease the amount of coated adhesive in order to increase the protrusion of the fine spheres, the basic adhesion properties become deteriorated, and is also not preferable.

[0049] On the other hand, when the average particle diameter exceeds about 50  $\mu\text{m}$ , the basic adhesion properties can become deteriorated, and thus the label floating or the like may occur.

[0050] Further, in terms of operation, fine spheres having a large particle diameter may be caught by a clearance when coating is performed using a gap clearance system, and thus a streak phenomenon can be easily caused, and it may be difficult to decrease the coating amount.

[0051] Although the increase of the coating amount of the adhesive changes the label floating for the better, it can effectuate various problems such as multidelamination over time, deterioration of specular oozing, defect in operating a printer, deterioration of the suitability for ink-jet recording, and the like, and thus is not preferable and disadvantageous in terms of the cost.

[0052] It may be preferable that the solid content of the fine spheres contained in the adhesive be about 10 to 90% by mass, and more preferably about 20 to 80% by mass, of the adhesive containing fine spheres. In this manner, by setting the solid content of the fine spheres within a range from about 10 to 90% by mass of the adhesive containing fine spheres, the linerless ink-jet recording adhesive label can exhibit both a stable light unwinding force and suitability for a curved surface that is a base of the adhesion properties. For example, when the content of the fine spheres is no less than 10% by mass, there is no concern about a defect in operating a printer

caused by increasing the unwinding force over time, deterioration of the suitability for ink-jet recording, and paper-tear occurring at worst. On the other hand, when the content is no more than 90% by mass, a good suitability for a curved surface can be maintained.

[0053] According to another exemplary embodiment of the present invention, the amount of the adhesive containing the fine spheres may preferably be about 5 to 50 g/m<sup>2</sup>, and more preferably about 10 to 30 g/m<sup>2</sup>, in dry weight. When the amount of the adhesive containing fine spheres is no less than 5 g/m<sup>2</sup>, the adhesion properties can be sufficiently exhibited when used as a label. On the other hand, when the amount is at most about 50 g/m<sup>2</sup>, there is little or no risk of causing problems such as multidelamination generated by a lack of protrusion of the fine spheres.

[0054] In order to form the adhesive layer, the adhesive containing the fine spheres can be coated onto the rear surface of the substrate. Although the adhesive used for coating may be either a solvent-based type or an emulsion type, the emulsion type adhesive is preferable, because the solvent-based type in which a solvent easily infiltrates into the ink-jet recording sheet may cause contamination of the ink-jet recording surface and deterioration of the suitability for ink-jet recording.

[0055] Even in the case of the emulsion type, when coating is performed using various applicators, it may be preferable that the viscosity be set as high as possible, so as to prevent the infiltration. It can be preferable that the emulsion type has a viscosity of approximately 100 to 15,000 mPas (25°C) and a concentration of about 20 to 80% in solid content, in order to control the amount of coating.

[0056] Coating of the adhesive containing the fine spheres can be performed using various applicators such as a Mayer bar coater, kiss roll coater, lip coater, direct roll coater, offset roll coater, gravure roll coater, reverse roll coater, rod coater, blade coater, comma direct coater, comma reverse coater, air knife coater, slit die coater, and the like. Drying can be performed in

accordance with a conventional method combined with the use of the above-mentioned applicators in accordance with the exemplary embodiment of the present invention.

[0057] It may be preferable that the adhesive containing the fine spheres be applied directly to the rear surface of the ink-jet recording sheet used as the substrate so as to exhibit sufficient adhesion properties to the substrate and to make the fine spheres sufficiently protrude out of the surface of the adhesive.

### Examples

[0058] Although the exemplary embodiments of the present invention will be more specifically explained by using Examples described below, the scope of the present invention is not limited by these examples. It should be understood that in the Examples, unless specifically stated otherwise, “%” and “parts” mean “% by mass” and “parts by mass”, respectively

#### Example 1

##### “Formation of Release Agent Layer”

[0059] An ink-jet recording sheet having a release agent layer was produced by using a high-quality paper (OTP 81.4 g/m<sup>2</sup>, manufactured by Oji Paper Co., Ltd.) as a substrate, and forming a release agent layer on one surface of the substrate by coating and hot-air drying polyvinyl alcohol containing a long-chain alkyl group (K-256, manufactured by CHUKYO YUSHI CO., LTD., the carbon-number of the long-chain alkyl group: 18) as a release agent using a gravure coater so that the amount of coating was 1.0 g/m<sup>2</sup>.

“Preparation of Adhesive Label”

[0060] A linerless ink-jet recording adhesive label was prepared by forming an adhesive layer on the rear surface of the ink-jet recording sheet having the above-formed release agent layer by mixing an acrylic emulsion adhesive (SVP-621TZ, manufactured by Saiden Chemical Industry) with fine spheres composed of an elastomer copolymer mainly containing acrylic acid ester (KPS-2004-3, the number-average particle diameter was 21 microns, manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD.) in a mass ratio of 50/50 equivalent to the solid content thereof and stirring the mixture, followed by coating and drying the mixture using a reverse roll coater so that the amount of coating was 15 g/m<sup>2</sup> in dry weight.

Example 2

[0061] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that the amount of coating of the release agent was 4.0 g/m<sup>2</sup> in “Formation of Release Agent Layer”.

Example 3

[0062] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that a release agent layer was formed onto the ink-jet recording surface using an ink-jet recording sheet with a coating layer (NIJ-115-1G, manufactured by Oji Paper Co., Ltd.) instead of the high-quality paper in “Formation of Release Agent Layer”.

#### Example 4

[0063] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that a release agent layer was formed onto the ink-jet recording surface using a foam sheet (OKHJ 64 g/m<sup>2</sup>, manufactured by Oji Paper Co., Ltd.) used instead of the high-quality paper in “Formation of Release Agent Layer”.

#### Example 5

##### “Formation of Release Agent Layer”

[0064] An ink-jet recording sheet having a release agent layer was produced in a similar manner to that of Example 1, except that polyvinyl alcohol containing a long-chain alkyl group (Pyroyl 406, manufactured by Ipposha Oil Industries Co., Ltd.) was used as a release agent in the same coating amount in “Formation of Release Agent Layer” of that example.

##### “Preparation of Adhesive Label”

[0065] A linerless ink-jet recording adhesive label was prepared by forming an adhesive layer on the rear surface of the ink-jet recording sheet having the above-formed release agent layer by mixing an acrylic emulsion adhesive (L-301, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) with fine spheres composed of an elastomer copolymer mainly containing acrylic acid ester (B-7772, the number-average particle diameter was 45 microns, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) in a mass ratio of 50/50 equivalent to the solid content thereof and stirring the mixture, followed by coating and drying the mixture using a reverse roll coater so that the amount of coating was 15 g/m<sup>2</sup> in dry weight.



Example 6

“Formation of Release Agent Layer”

[0066] An ink-jet recording sheet having a release agent layer was produced in a similar manner to that of Example 1, except that polyvinyl alcohol containing a long-chain alkyl group (M-479, manufactured by CHUKYO YUSHI CO., LTD., the carbon-number of the long-chain alkyl group: 18) was used in the same coating amount in “Formation of Release Agent Layer” of that example.

“Preparation of Adhesive Label”

[0067] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that an adhesive layer was formed on the rear surface of the ink-jet recording sheet having the above-formed release agent layer by mixing the acrylic emulsion adhesive (L-301, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) with the fine spheres (B-7772, the number-average particle diameter was 45 microns, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) in a mass ratio of 75/25 equivalent to the solid content thereof and stirring the mixture, followed by coating and drying the mixture using a reverse roll coater so that the amount of coating was 15 g/m<sup>2</sup> in dry weight.

Example 7

[0068] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that the acrylic emulsion adhesive (L-301, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) was mixed and stirred with the fine spheres (B-7772, the number-average particle diameter was 45 microns, manufactured by NIPPON CARBIDE

INDUSTRIES CO., INC.) in a mass ratio of 25/75 equivalent to the solid content thereof in  
“Preparation of Adhesive Label” of that example.

#### Example 8

5    **[0069]**       A linerless ink-jet recording adhesive label was prepared in a similar manner to that  
of Example 1, except that the acrylic emulsion adhesive (L-301, manufactured by NIPPON  
CARBIDE INDUSTRIES CO., INC.) was mixed and stirred with fine spheres composed of an  
elastomer copolymer mainly containing acrylic acid ester (B-7747, the number-average particle  
diameter was 33 microns, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) in a  
10   mass ratio of 75/25 equivalent to the solid content thereof in “Preparation of Adhesive Label” of  
that example.

#### Example 9

**[0070]**       A linerless ink-jet recording adhesive label was prepared in a similar manner to that  
15   of Example 1, except that the acrylic emulsion adhesive (L-301, manufactured by NIPPON  
CARBIDE INDUSTRIES CO., INC.) was mixed and stirred with the fine spheres (B-7772, the  
number-average particle diameter was 45 microns, manufactured by NIPPON CARBIDE  
INDUSTRIES CO., INC.) in a mass ratio of 10/90 equivalent to the solid content thereof and the  
amount of coating was 20 g/m<sup>2</sup> in dry weight in “Preparation of Adhesive Label” of that example.

20

Example 10

[0071] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that an acrylic emulsion adhesive (TS-662L, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) was mixed and stirred with the fine spheres (B-7772, the number-average particle diameter was 45 microns, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) in a mass ratio of 80/20 equivalent to the solid content thereof and the amount of coating was 20 g/m<sup>2</sup> in dry weight in “Preparation of Adhesive Label” of that example.

Example 11

[0072] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that an acrylic emulsion adhesive (SVP-621TZ, manufactured by Saiden Chemical Industry) was mixed and stirred with the fine spheres (KPS-2004-3, the number-average particle diameter was 21 microns, manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD.) in a mass ratio of 90/10 equivalent to the solid content thereof in “Preparation of Adhesive Label” of that example.

Comparative Example 1

[0073] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that a high-quality paper (OTP 64 g/m<sup>2</sup>, manufactured by Oji Paper Co., Ltd.) was used as a substrate and on one surface of which a release agent layer was formed by coating and hot-air drying a silicone resin (a mixture in which 1 part by mass of SRX-212 containing a platinum catalyst was mixed with 100 parts by mass of SD7220, manufactured by

Dow Corning Toray Silicone Co. Ltd.) as a release agent using a gravure coater so that the amount of coating was 1.5 g/m<sup>2</sup> in “Formation of Release Agent Layer” of that example.

#### Comparative Example 2

5    [0074]        A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that a high-quality paper (OTP 81.4 g/m<sup>2</sup>, manufactured by Oji Paper Co., Ltd.) was used as a substrate and on one surface of which a release agent layer was formed by coating and hot-air drying a silicone resin (a mixture in which 5 parts by mass of CAT-PM-10A containing a platinum catalyst was mixed with 100 parts by mass of X-52-195, manufactured by  
10   Shin-Etsu Chemical Co., Ltd.) as a release agent using a gravure coater so that the amount of coating was 1.0 g/m<sup>2</sup> in “Formation of Release Agent Layer” of that example.

#### Comparative Example 3

[0075]        A linerless ink-jet recording adhesive label was prepared in a similar manner to that  
15   of Example 1, except that an adhesive layer was formed without using fine spheres by coating and drying an acrylic emulsion adhesive (SVP-621TZ, manufactured by Saiden Chemical Industry) as an adhesive using a reverse roll coater so that the amount of coating was 12 g/m<sup>2</sup> in dry weight in “Preparation of Adhesive Label” of that example.

#### 20   Comparative Example 4

[0076]        A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that an adhesive layer was formed without using fine spheres by coating and

drying an acrylic emulsion adhesive (TS-662L, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) as an adhesive using a reverse roll coater so that the amount of coating was 12 g/m<sup>2</sup> in dry weight in “Preparation of Adhesive Label” of that example.

5 Comparative Example 5

[0077] A linerless ink-jet recording adhesive label was prepared in a similar manner to that of Example 1, except that an adhesive layer was formed without using fine spheres by coating and drying an acrylic emulsion adhesive (TS-662L, manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) as an adhesive using a reverse roll coater so that the amount of coating was 22 g/m<sup>2</sup> in dry weight in “Preparation of Adhesive Label” of that example.

[0078] Sixteen kinds of the linerless ink-jet recording adhesive labels obtained as described above were evaluated with respect to the following items. Results thereof are shown in Table 1. The method for evaluating with respect to each item is described below.

15 (Unwinding Force)

[0079] In accordance with JIS Z 0237, the unwinding force of the respective linerless ink-jet recording adhesive label was measured at a peel rate of 5 m/min or 20 m/min after the treatment in an environment at 23°C and 50% RH (relative humidity) for 7 days or at 40°C and 50% RH for 1 month, and evaluated in accordance with the following criteria.

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◎: The peel force was no more than 20 N/m and peeling was performed with little resistance.

○: The peel force was over 20 N/m and no more than 30 N/m, and peeling was performed well.

5 △: The peel force was over 30 N/m and no more than 50 N/m, and peeling was performed with a slight resistance but there was no practical problem.

×: The peel force was over 50 N/m and peeling was performed with a severe resistance or the adhesive label was torn.

10 (Adhesion Force)

[0080] In accordance with JIS Z 0237, the adhesion force of the respective linerless ink-jet recording adhesive label to polyethylene or high-quality paper was measured at a peel rate of 0.3 m/min in an environment at 23°C and 50% RH.

15 [Suitability for curved surface]

[0081] After the respective linerless ink-jet recording adhesive label was treated in an environment at 23°C and 50% RH for 7 days (1) or at 40°C and 50% RH for 1 month (2), the label with a width of 15 mm and a length of 20 mm was wound around a 50 mm□ pipe (made from polyethylene), left in an environment at 23°C and 50% RH for 1 day, and measured with respect to  
20 the unstuck length of both end portions thereof to evaluate in accordance with the following criteria.

- ⊙: The unstuck length of both end portions was no more than 2 mm.
- : The unstuck length of both end portions was no more than 4 mm.
- △: The unstuck length of both end portions was no more than 6 mm.
- ×: The unstuck length of both end portions was more than 6 mm.

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[Ink-absorbability (repellent property)]

[0082] The respective linerless ink-jet recording adhesive label was subjected to printing using an ink-jet printer (PM-670C, manufactured by SEIKO EPSON CORPORATION), and the state of the printed portion was evaluated with respect to the ink-droplet repellency in accordance with the following criteria.

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- ⊙: Repelled ink-droplets were not recognized.
- : Although repelled ink-droplets were slightly recognized in printed thin lines, there was no practical problem.
- △: Although repelled ink-droplets were partially recognized in printed letters, the letters could be sufficiently read and there was no practical problem.
- ×: Repelled ink-droplets were significantly recognized, and the external appearance of the letters was poor.

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[Ink-drying Property]

[0083] The respective linerless ink-jet recording adhesive label was subjected to printing using an ink-jet printer (PM-670C, manufactured by SEIKO EPSON CORPORATION), and the

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printed portion was immediately rubbed with fingers to evaluate the drying property in accordance with the following criteria.

○: The printed portion was completely dried.

△: Although the printed portion was slightly undried immediately after printing, it was  
5 completely dried after a few seconds, and there was no practical problem.

×: The printed portion was almost undried.

Table 1

	20 m/min Unwinding Force (N/m)		5 m/min Unwinding Force (N/m)		Adhesion Force(N/m)	
	23°C, 50% RH	40°C, 50% RH 1 Month	23°C, 50% RH	40°C, 50% RH 1 Month	To Polyethylene	To High-quality Paper
Example 1	◎(15)	△(38)	◎(19)	△(42)	85	187
Example 2	◎(7)	○(22)	◎(10)	○(29)	83	187
Example 3	◎(17)	○(28)	○(24)	△(34)	72	174
Example 4	◎(15)	△(34)	○(21)	△(39)	90	196
Example 5	◎(12)	○(22)	○(21)	○(28)	82	180
Example 6	◎(12)	△(23)	◎(19)	○(30)	104	232
Example 7	◎(5)	◎(12)	◎(8)	◎(18)	50	122
Example 8	◎(18)	△(44)	○(26)	△(48)	125	266
Example 9	◎(3)	◎(10)	◎(10)	◎(14)	14	20
Example 10	◎(10)	◎(18)	◎(15)	○(22)	72	191
Example 11	○(26)	△(46)	△(31)	△(49)	246	Paper Tears
Comparative Example 1	◎(2)	◎(6)	◎(1)	◎(2)	85	189
Comparative Example 2	◎(8)	○(23)	◎(5)	◎(18)	87	186
Comparative Example 3	○(29)	×(56)	△(40)	×(60)	250	Paper Tears
Comparative Example 4	○(21)	△(40)	△(31)	△(43)	38	155
Comparative Example 5	○(26)	×(54)	△(38)	×(56)	140	237



Table 1 (Continued)

	Suitability for Curved Surface (Unstuck Length : mm)		Ink-absorbability	Ink-drying Property
	23°C, 50% RH	40°C, 50% RH 1 Month		
Example 1	◎(0)	◎(0)	◎	◎
Example 2	◎(0)	◎(0)	○	△
Example 3	◎(1)	◎(1)	◎	◎
Example 4	◎(0)	◎(1)	◎	◎
Example 5	◎(0)	◎(1)	◎	◎
Example 6	◎(0)	◎(0)	◎	◎
Example 7	○(3)	○(3)	◎	◎
Example 8	○(3)	○(3)	◎	◎
Example 9	△(5)	△(5)	◎	◎
Example 10	○(3)	△(5)	◎	◎
Example 11	◎(0)	◎(0)	◎	◎
Comparative Example 1	◎(0)	◎(0)	×	×
Comparative Example 2	◎(1)	○(3)	×	△
Comparative Example 3	◎(0)	◎(1)	◎	○
Comparative Example 4	△(5)	×(9)	◎	◎
Comparative Example 5	○(3)	△(6)	◎	△

[0084] As is apparent from Table 1, Comparative Examples 1 and 2 in which the respective silicone resins were used as the release agent thereof resulted in a lack of both the  
5 ink-absorbability and ink-drying property.

[0085] Comparative Examples 3 to 5 are examples in which the respective adhesive layer was formed using only the adhesive without using fine particles in preparation of the respective adhesive label. It is apparent that in Comparative Example 3 in which the adhesive having a relatively strong adhesion force was used, the unwinding force after the treatment performed in an

environment at 40°C and 50% RH for 1 month was excessively strong. It is apparent that Comparative Example 4 in which the adhesive having a relatively weak adhesion force was used resulted in a defective suitability for a curved surface after being left for 1 month. It is apparent that in Comparative Example 5 in which the amount of the adhesive was increased in order to  
5 improve the suitability for a curved surface, the suitability for a curved surface after being left for 1 month was improved, but the unwinding force (20 m/min) after the treatment performed in an environment at 40°C and 50% RH for 1 month was deteriorated. That is, it is apparent that it was difficult for the labels to exhibit both the adhesion properties and the peeling properties when unwound by using only a polyvinyl alcohol containing a long-chain alkyl group as a release agent.

10 [0086] In contrast, it is apparent that the linerless adhesive labels according to the exemplary embodiments of the present invention had both the adhesion properties and peeling properties free from practical problems. In Table 1, the linerless adhesive label of Example 9 exhibited a low value of the adhesion force in itself. However, the suitability for a curved surface of this adhesive label was free from practical problems, probably because this adhesive label used  
15 the mixture of the adhesive and the fine spheres for the adhesive layer and the fine spheres could create a sufficient adhesive-contact area by elastic deformation when stuck to the curved surface or the like.

[0087] Although the adhesives of Example 11 and Comparative Example 3 caused the paper to tear in the measurement of the adhesion force to the high-quality paper, there seemed to be  
20 no practical problems because the paper-tear itself occurred when peeling off a label after the end of use of the label.

#### Industrial Applicability

[0088] The adhesive label of the present invention does not require a release paper and is  
25 used for intended purposes suitable for ink-jet printing.

[0089] According to the exemplary embodiments of the present invention, a linerless ink-jet recording adhesive label can be provided which does not require a release paper, has suitability for ink-jet recording, does not cause an increase of the peel force even over time, and is excellent in the adhesion and peeling properties.

5 [0090] The foregoing merely illustrates the exemplary principles of the present invention. Various modifications and alterations to the described embodiments will be apparent to those skilled in the art in view of the teachings herein. It will thus be appreciated that those skilled in the art will be able to devise numerous modification to the exemplary embodiments of the present invention which, although not explicitly shown or described herein, embody the principles of the  
10 invention and are thus within the spirit and scope of the invention. All publications, applications and patents cited above are incorporated herein by reference in their entirety.

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